

DESCRIPTION

METHOD FOR PRODUCING Ti OR Ti ALLOY THROUGH REDUCTION BY Ca

5 TECHNICAL FIELD

[0001] The present invention relates to a method for producing Ti or Ti alloys through reduction by Ca, in which a metallic chloride containing titanium tetrachloride (TiCl_4) is reduced by Ca to produce Ti metals or Ti alloys.

10 BACKGROUND ART

[0002] A Kroll method for reducing TiCl_4 by Mg is generally used as an industrial production method of the titanium metals. In the Kroll method, the Ti metals are produced through a reduction step and a vacuum separation step. In the reduction step, TiCl_4 which is of a raw material of Ti is reduced in a reactor vessel to produce the sponge metallic Ti. In the vacuum separation step, unreacted Mg and magnesium chloride (MgCl_2) formed as by-products are removed from the sponge metallic Ti produced in the reactor vessel.

[0003] The reduction step will be described in detail. In this step, the reactor vessel is filled with the molten Mg, and the TiCl_4 liquid is supplied from above on a liquid surface of the molten Mg. This allows TiCl_4 to be reduced by Mg near the liquid surface of the molten Mg to generate the particulate metallic Ti. The generated Ti metals move sequentially downward. At the same time, the molten MgCl_2 which is of the by-product is generated near the liquid surface. A specific gravity of molten MgCl_2 is larger than that of the molten Mg. The molten MgCl_2 which is of the by-product moves downward due to the specific gravity difference, and the molten Mg emerges in the liquid surface instead. The molten Mg is continuously supplied to the liquid surface by the specific gravity difference substitution, and the reducing reaction of TiCl_4 proceeds continuously.

[0004] In the Ti metal production by the Kroll method, a high-purity product is produced. However, a production cost is increased and the product becomes remarkably expensive. One of factors of increased production cost is the difficulty in enhancing a feed rate of TiCl_4 . The following three items are cited
5 as the reason why the feed rate of TiCl_4 is restricted.

[0005] In order to improve productivity in the Kroll method, it is effective to increase the feed rate of TiCl_4 which is of the raw material of Ti, i.e., to increase a supply amount of molten Mg to the liquid surface per unit area or unit time. However, when the feed rate of TiCl_4 is excessively increased, the
10 specific-gravity difference substitution cannot keep up with the reaction rate, so that while MgCl_2 remains in the liquid surface, TiCl_4 is supplied to the MgCl_2 . As a result, the supplied TiCl_4 becomes lower grade chloride gases (referred to as "unreacted gas") such as an unreacted TiCl_4 gas and a TiCl_3 gas, and the unreacted gas is discharged outside the reactor vessel, which reduces
15 utilization efficiency of TiCl_4 . It is necessary to avoid the generation of the unreacted gas, because a rapid increase in inner pressure of the reactor vessel is associated with the generation of the unreacted gas. Thus, there is a limit of the feed rate of TiCl_4 because of the above reasons.

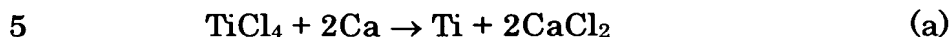
[0006] When the feed rate of TiCl_4 is enhanced, Mg vapor generated from the
20 liquid surface of the molten Mg reacts with TiCl_4 vapor to increase a precipitation amount of Ti in the inner surface of the reactor vessel above the liquid surface of the molten Mg. On the other hand, the liquid surface of the molten Mg rises as the reducing reaction proceeds. Therefore, the precipitated Ti in the inner surface of the upper portion of the reactor vessel is immersed in
25 the molten Mg at a late stage of the reducing reaction, which causes the effective area of the Mg liquid surface to be decreased to reduce the reaction rate. In order to suppress the decrease of reaction rate, it is necessary that the feed rate of TiCl_4 be restricted to prevent the Ti precipitation in the inner surface of the upper portion of the reactor vessel.

[0007] Therefore, Japanese Patent Application Publication No. 8-295955 proposes a method in which the reaction efficiency is enhanced by supplying liquid TiCl_4 in a dispersive manner to the liquid surface in which the molten Mg exists, and thereby the Ti precipitation is suppressed in the inner surface of the upper portion of the reactor vessel. However, the method proposed in Japanese Patent Application Publication No. 8-295955 is not enough to suppress the Ti precipitation. In the Kroll method, because the reaction is performed only near the liquid surface of the molten Mg in the reactor vessel, an exothermic area is narrowed and the temperature is locally elevated. Therefore, cooling becomes difficult, so that the feed rate of TiCl_4 is restricted.

[0008] Although the feed rate of TiCl_4 is not directly affected, in the Kroll method, Ti is generated in the particulate form near the liquid surface of the molten Mg liquid, and moves downward. However, because of wetting properties (adhesion properties) of the molten Mg, the generated Ti powder moves downward while aggregated, and the Ti particles are sintered to grow the Ti particles in size by the temperature condition of the molten liquid during moving downward, which makes it difficult to discharge the Ti particles outside the reactor vessel. Therefore, the continuous production is difficult to perform, and the improvement of the productivity is blocked. This is the reason why the Ti is produced in the batch manner in the form of the sponge titanium by the Kroll method.

[0009] With reference to the Ti production methods except for the Kroll method, for example, US Patent No. 2205854 describes that, in addition to Mg, for example, Ca can be used as the reducing agent of TiCl_4 . US Patent No. 4820339 describes a method for producing Ti through the reducing reaction by Ca, in which the molten salt of CaCl_2 is held in the reactor vessel, the metallic Ca powder is supplied into the molten salt from above, Ca is dissolved in the molten salt, and TiCl_4 gas is supplied from below to react the dissolved Ca with TiCl_4 in the molten salt of CaCl_2 .

[0010] In the reduction by Ca, the Ti metals are generated from TiCl_4 by the reaction of the following chemical formula (a), and CaCl_2 as the by-product is also generated at the same time. Ca has a stronger affinity for Cl stronger than Mg has, and Ca is suitable for the reducing agent of TiCl_4 in principle.



[0011] Particularly, in the method described in US Patent No. 4820339, Ca is used while dissolved in the molten CaCl_2 . When the reducing reaction by Ca is utilized in the molten CaCl_2 , a reaction field is enlarged compared with the Kroll method in which TiCl_4 is supplied to the liquid surface of the reducing
10 agent in the reactor vessel and the reaction field is limited to near the liquid surface. Therefore, because the exothermic area is also enlarged to facilitate the cooling, the feed rate of TiCl_4 which is of the raw material of Ti can be largely increased, and the remarkable improvement of the productivity can be also expected.

15 [0012] However, it is difficult that the method described in US Patent No. 4820339 is adopted as the industrial Ti production method. When using the metallic Ca powder as the reducing agent, since the metallic Ca powder is extremely expensive, the production cost is higher than that of the Kroll method in which the feed rate of TiCl_4 is restricted. In addition, the highly
20 reactive Ca is extremely difficult to handle, which can also be the factor of blocking the industrial application of the method for producing Ti through the reduction by Ca.

[0013] An example of other Ti production methods includes an Olsen method described in US Patent No. 2845386. The Olsen method is a kind of oxide
25 direct-reduction method for directly reducing TiO_2 by Ca, in which TiO_2 is directly reduced by Ca, not through TiCl_4 . Although the oxide direct-reduction method is highly efficient, the oxide direct-reduction method is not suitable for the production of the high-purity Ti because it is necessary to use high-purity TiO_2 .

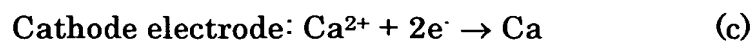
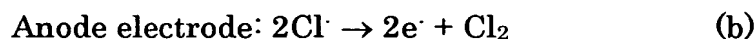
DISCLOSURE OF THE INVENTION

[0014] It is an object of the present invention to provide a method for economically producing high-purity Ti metals or high-purity Ti alloys with high efficiency without using an expensive reducing agent.

[0015] In order to achieve the above object, the present inventors consider that TiCl_4 be reduced by Ca, and the present inventors look into the method for utilizing Ca dissolved in the molten salt of CaCl_2 described in US Patent No. 4820339.

In the method described in US Patent No. 4820339, Ca in the molten salt is consumed in the reducing reactor vessel as the reaction expressed by the chemical formula (a) proceeds, and it is necessary to continuously supply the metallic Ca powder to the reducing reactor vessel. However, in order to industrially establish the method for producing Ti through reduction by Ca, the present inventors focus on a method for controlling a dissolved Ca concentration in the molten salt by electrolysis in consideration of the fact that it is necessary that the Ca consumed in the reducing reaction is economically replenished into the molten salt.

[0016] That is, when the molten CaCl_2 is electrolyzed in a reactor cell, electrode reactions expressed by the following chemical formulas (b) and (c) proceed to generate a Cl_2 gas near the surface of an anode electrode while generating Ca near the surface of a cathode electrode, which allows the Ca concentration to be increased in the molten salt. Therefore, when TiCl_4 is supplied to CaCl_2 so as to react with Ca generated on the anode electrode side, because Ca consumed in the Ti generation is replenished as needed, the replenishment of metallic Ca from the outside or extraction of metallic Ca becomes unnecessary, which allows the Ti metals to be economically produced.



[0017] The method for replenishing Ca consumed by the reduction of TiCl_4 with Ca generated by the electrolysis can also be achieved by respectively performing the reduction and the electrolysis in a reducing cell and an electrolytic cell to circulate the molten CaCl_2 between the cells. However, when TiCl_4 is supplied to the molten CaCl_2 in the reactor cell so as to react with Ca generated on the cathode electrode side by the electrolysis, the reactor cell can commonly be used as the reducing cell and the electrolytic cell. Therefore, because it is not necessary to separately provide the reducing cell and the electrolytic cell, there is a great advantage from a viewpoint of installation cost compared with the case in which the molten CaCl_2 is circulated between the reducing cell and the electrolytic cell.

[0018] The present invention is made based on the above consideration, and the summary of the present invention is a method for producing Ti or Ti alloys through reduction by Ca according to the following (1) to (7).

(1) A method for producing Ti or Ti alloys through reduction by Ca, including: a reduction electrolysis step in which a molten salt is held in a reactor cell to perform electrolysis in the molten salt of the reactor cell, the molten salt containing CaCl_2 while Ca being dissolved in the molten salt and Ti or Ti alloys are generated in the molten salt by supplying a metallic chloride containing TiCl_4 into the molten salt in order to cause the metallic chloride containing TiCl_4 to react with Ca generated on a cathode electrode side by the electrolysis; and a Ti separation step of separating the Ti or Ti alloys from the molten salt inside the reactor cell or outside the reactor cell, in which the reactor cell is provided with a membrane which partitions an inside of the reactor cell into an anode electrode side and the cathode electrode side, the membrane blocking the movement of Ca generated on the cathode electrode side in the reactor cell to the anode electrode side while permitting the molten salt to flow in the reactor cell (hereinafter referred to as "production method described in (1)").

[0019] (2) A method for producing Ti or Ti alloys through reduction by Ca, including: a reduction electrolysis step in which a molten salt is held in a reactor cell to perform electrolysis using an electroconductive porous material as an cathode electrode in the molten salt of the reactor cell, the molten salt containing CaCl_2 while Ca being dissolved in the molten salt, and Ti or Ti alloys are generated in the molten salt by supplying a metallic chloride containing TiCl_4 into the molten salt through the cathode electrode in order to cause the metallic chloride containing TiCl_4 to react with Ca generated on a cathode electrode side by the electrolysis; and a Ti separation step of separating the Ti or Ti alloys from the molten salt inside the reactor cell or outside the reactor cell (hereinafter referred to as "production method described in (2)").

[0020] (3) A method for producing Ti or Ti alloys through reduction by Ca, including: a reduction electrolysis step in which a molten salt is held in a reactor cell to perform electrolysis in the molten salt of the reactor cell, the molten salt containing CaCl_2 while Ca being dissolved in the molten salt, and Ti or Ti alloys are generated in the molten salt by supplying a metallic chloride containing TiCl_4 into the molten salt in order to cause the metallic chloride containing TiCl_4 to react with Ca generated on a cathode electrode side by the electrolysis; a Ti separation step of separating the Ti or Ti alloys from the molten salt inside the reactor cell or outside the reactor cell; and a chlorination step of causing Cl_2 to react with TiO_2 to generate TiCl_4 , Cl_2 being generated on an anode electrode side in association with the electrolysis, in which TiCl_4 generated in the chlorination step is used for the Ti or Ti alloy generation reaction in the reactor cell (hereinafter referred to as "production method described in (3)").

[0021] (4) A method for producing Ti or Ti alloys through reduction by Ca, including: a reduction electrolysis step in which a molten salt is held in a reactor cell to perform electrolysis in the molten salt of the reactor cell, the molten salt containing CaCl_2 while Ca being dissolved in the molten salt, and

Ti or Ti alloys are generated in the molten salt by supplying a metallic chloride containing TiCl_4 into the molten salt in order to cause the metallic chloride containing TiCl_4 to react with Ca generated on a cathode electrode side by the electrolysis; and a Ti separation step in which Ti or Ti alloys generated in the reactor cell are extracted to an outside of the reactor cell along with the molten salt and the Ti or Ti alloys are separated from the molten salt outside the reactor cell (hereinafter referred to as "production method described in (4)").

[0022] (5) A method for producing Ti or Ti alloys through reduction by Ca, including: a reduction electrolysis step in which a multi-system molten salt is held in a reactor cell to perform electrolysis in the molten salt of the reactor cell, the multi-system molten salt containing at least one of NaCl, KCl, LiCl, and CaF_2 in addition to CaCl_2 , Ca being dissolved in the molten salt, and Ti or Ti alloys are generated in the molten salt by supplying a metallic chloride containing TiCl_4 into the molten salt in order to cause the metallic chloride containing TiCl_4 to react with Ca generated on a cathode electrode side by the electrolysis; and a Ti separation step of separating the Ti or Ti alloys from the molten salt inside the reactor cell or outside the reactor cell (hereinafter referred to as "production method described in (5)").

[0023] (6) A method for producing Ti or Ti alloys through reduction by Ca, including: a reduction electrolysis step in which a molten salt is held in a reactor cell to perform electrolysis in the molten salt in the reactor cell, the molten salt containing CaCl_2 while Ca being dissolved in the molten salt, and Ti or Ti alloys are generated in the molten salt by supplying a mixed gas containing TiCl_4 and another metallic chloride into the molten salt in order to cause the mixed gas to react with Ca generated on a cathode electrode side by the electrolysis; and a Ti separation step of separating the Ti or Ti alloys from the molten salt inside the reactor cell or outside the reactor cell (hereinafter referred to as "production method described in (6)").

[0024] (7) A method for producing Ti or Ti alloys through reduction by Ca,

including: a reduction electrolysis step in which a molten salt is held in a reactor cell to perform electrolysis in the molten salt of the reactor cell, the molten salt containing CaCl_2 while Ca being dissolved in the molten salt, and Ti or Ti alloys are generated in the molten salt by supplying a metallic chloride containing TiCl_4 into the molten salt in order to cause the metallic chloride containing TiCl_4 to react with Ca generated on a cathode electrode side by the electrolysis, said Ti or Ti alloys being formed in powder whose average particle size ranging from 0.5 to 50 μm ; and a Ti separation step of separating the Ti or Ti alloys from the molten salt inside the reactor cell or outside the reactor cell (hereinafter referred to as "production method described in (7)").

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] Fig. 1 is a view showing a relationship between a mixture ratio and a melting point in a binary-system mixed molten salt of CaCl_2 and NaCl ;

Fig. 2 is a block diagram showing a Ti metal production apparatus to which a first embodiment mode according to the present invention can be applied;

Fig. 3 is a block diagram showing a Ti metal production apparatus to which a second embodiment mode according to the present invention can be applied; and

Fig. 4 is a block diagram showing a Ti metal production apparatus to which a third embodiment mode according to the present invention can be applied.

BEST MODE FOR CARRYING OUT THE INVENTION

[0026] 1. Contents of the Method according to the Invention (Production Methods Described in (1) to (7))

In each of the methods according to the present invention for producing Ti or Ti alloys through the reduction by Ca, for example, the molten

CaCl₂ which is of the molten salt is held in the reactor cell. When TiCl₄ is supplied to the molten salt in the reactor cell, TiCl₄ is reduced by Ca dissolved in the molten salt, and the particulate and/or powdery metallic Ti (hereinafter referred to as "Ti particles") is generated. Although Ca dissolved in the molten salt is consumed in association with the generation of the Ti particles, because the electrolysis of the molten CaCl₂ progresses in conjunction with the reducing reaction in the reactor cell, Ca is generated on the cathode electrode side and the dissolved Ca which is consumed in the reducing reaction is replenished with Ca generated by the electrolysis. Therefore, the metallic Ca replenishment operation and the metallic Ca extraction operation are not required while the Ti particles are continuously produced.

[0027] Conventionally one of the main reasons why Ca is not used in the industrial production of the Ti metals is the difficulty in separating Ca and CaCl₂. Mg is produced by electrolyzing MgCl₂, and the generated Mg can efficiently be recovered because Mg is hardly dissolved in MgCl₂. Similarly to Mg, Na can efficiently be produced by electrolyzing NaCl. On the other hand, Ca is produced by electrolyzing CaCl₂, and the generated Ca is dissolved in CaCl₂ by about 1.5%.

[0028] Therefore, it is difficult to efficiently produce only Ca. In addition, there is also a phenomenon in which the dissolved Ca generates CaCl₂ by a back reaction (reaction in which Ca generated on the cathode electrode side is bonded to Cl₂ generated on the anode electrode side to return to CaCl₂), so that the production efficiency of Ca becomes worsened. For example, the improvement of a recovery factor of Ca is performed by cooling an electrode. However, the production cost of Ca is still high.

However, in the method for producing Ti or Ti alloys through the reduction by Ca according to the present invention, Ca dissolved in the molten CaCl₂ is used and the Ca separation is not required, so that the Ca electrolytic production cost can be decreased.

[0029] When the Ca reduction in the molten salt is utilized, the reducing reaction field is expanded and the heat generation area is simultaneously enlarged. Mg has vapor pressure of 6.7 kPa (50 mmHg) at 850 °C while Ca has extremely small vapor pressure of 0.3 kPa (2 mmHg). Therefore, in the case where Ca is used for the reduction process, the Ti precipitation amount becomes dramatically lessened in the inner surface of the upper portion of the reactor cell when compared with the use of Mg. Accordingly, in the method for producing Ti or Ti alloys through the reduction by Ca according to the present invention, the TiCl_4 feed rate can be largely increased.

In addition, Ca is inferior in wetting properties (adhesion properties) to Mg, and Ca adhering to the precipitated Ti particles is dissolved in CaCl_2 , so that the particle growth caused by the aggregation and the sintering in the generated titanium particles are significantly lessened. Therefore, the generated Ti can be discharged in the form of particles from the reactor cell, and the Ti production can continuously be operated.

[0030] For a supply mode of TiCl_4 to the molten CaCl_2 liquid, it is particularly desirable that TiCl_4 be directly supplied in the gas state into the molten CaCl_2 liquid because of higher contact efficiency of TiCl_4 with Ca in the molten CaCl_2 liquid. However, the TiCl_4 supply mode is not limited to the one in which TiCl_4 in the gas state is supplied. For example, it is also possible that either the liquid or gaseous TiCl_4 is supplied to the liquid surface of the molten CaCl_2 liquid, or it is also possible that either the liquid or gaseous TiCl_4 is supplied to either the liquid surface or the inside of the molten Ca liquid held on the molten CaCl_2 liquid.

[0031] In the case where the reducing reaction is generated by supplying the TiCl_4 liquid to the surface of the molten Ca liquid held on the molten CaCl_2 liquid, it is desirable that the molten Ca liquid be held in a thin state to an extent in which Ca in the molten CaCl_2 liquid can be utilized. When the Ca layer is thin, because Ca in the molten CaCl_2 liquid is involved in the reaction,

the reaction can range from the molten Ca layer to the molten CaCl_2 layer to continue the Ti generation even if the specific-gravity difference substitution becomes unable to keep up with it due to the increase in the TiCl_4 feed rate.

[0032] For the supply of TiCl_4 gas, the method for producing Ti or Ti alloys through the reduction by Ca according to the present invention has various advantages compared with the Kroll method.

That is, in the Kroll method, the TiCl_4 liquid is supplied to the liquid surface of the molten Mg liquid, and it has been tried that the TiCl_4 gas is supplied into the molten Mg liquid in order to enlarge the reaction field. However, as described above, since the Mg has the large vapor pressure, the Mg vapor intrudes in a supply nozzle to react with TiCl_4 , and the supply nozzle is choked.

[0033] Meanwhile, it has been tried that the TiCl_4 gas is supplied into the molten MgCl_2 liquid. However, the nozzle choking problem still remains although a choking frequency of the supply nozzle is decreased. This is because sometimes the melt is stirred by the bubbling of the TiCl_4 gas to cause the molten Mg to reach the supply nozzle. Even if TiCl_4 is supplied to the molten MgCl_2 liquid, the reducing reaction is difficult to occur because Mg is hardly dissolved in the melt.

[0034] On the contrary, in the method of utilizing the Ca reduction, the nozzle choking is hardly generated, and the TiCl_4 gas can be supplied into the molten CaCl_2 liquid. The reason why the nozzle choking is hardly generated is attributed to the fact that the molten Ca has the small vapor pressure.

That is, the method for producing Ti or Ti alloys through the reduction by Ca according to the present invention, it is particularly desirable that TiCl_4 be directly supplied in the gas state to the molten CaCl_2 liquid, and this supply mode can be applied without any problem in the actual operation. It is also possible to adopt the supply mode in which either the liquid or gaseous TiCl_4 is supplied to the liquid surface of the molten CaCl_2 liquid or to the liquid

surface or the inside of the molten Ca liquid held on the molten CaCl_2 liquid.

[0035] In the method for producing Ti or Ti alloys through the reduction by Ca according to the present invention, the Ti particles generated in the molten CaCl_2 liquid can be separated from the molten CaCl_2 liquid either in the reactor cell or outside the reactor cell.

However, when the separation is performed in the reactor cell, the production mode becomes the batch manner. In order to improve the productivity, the Ti particles and the molten CaCl_2 liquid can be separated from each other outside the reactor cell by utilizing the Ti generated in the particulate form to discharge the Ti particles outside the reactor cell along with the molten CaCl_2 liquid. This step is included as the Ti separation step in the production method described in (4). According to the production method described in (4), the Ti particles can simply be separated from the molten salt by a squeezing operation by means of mechanical compression.

[0036] For handling Cl_2 generated by the electrolysis, as stipulated by the production method described in (3), desirably Cl_2 is caused to react with TiO_2 to generate TiCl_4 , and the TiCl_4 is used for the Ti or Ti alloy generation reaction in the reactor cell.

[0037] In the case where Ti is produced by the method according to the present invention, TiCl_4 is used as the raw material. However, the Ti alloy can also be produced by mixing TiCl_4 and other metallic chloride. Because TiCl_4 and other metallic chloride are simultaneously reduced by Ca, the Ti alloy particles can be produced by this method.

[0038] TiCl_4 and other metallic chloride may be used in either the gas state or the liquid state. However, as stipulated by the production method described in (6), because of higher contact efficiency of TiCl_4 with Ca in the molten CaCl_2 liquid, desirably TiCl_4 and other metallic chloride are used in the mixed gas containing TiCl_4 and other metallic chloride is used.

[0039] In the method according to the present invention for producing Ti or

Ti alloys through the reduction by Ca, there are problems such as the back reaction and the reactor material wastage. In the back reaction, Ca (Ca generated on the cathode electrode side or the unreacted Ca) in the molten CaCl_2 are bonded to Cl_2 generated on the anode electrode side, and Ca returns to CaCl_2 . The reactor material wastage is caused by the high reactivity of Ca. When the back reaction is generated, the current efficiency is decreased because the electrolytic current is consumed for the back reaction.

As stipulated by the production method described in (1), the back reaction problem, particularly the back reaction in which Ca generated on the cathode electrode side is bonded to Cl_2 generated on the anode electrode side can effectively be suppressed by using a reactor cell including a membrane which partitions the electrolytic cell into the anode electrode side and the cathode electrode side. The reactor cell holds the molten salt, and the membrane permits the molten salt to be circulated in the electrolytic cell while blocking the movement of Ca generated on the cathode electrode side to the anode electrode side in the reactor cell.

[0040] On the other hand, to address the problem of the reactor material wastage, it is effective that the molten salt is not formed by the single CaCl_2 but formed by a mixed salt so that a melting point of the molten salt is decreased to lower the molten salt temperature (namely bath temperature). That is, as stipulated by the production method described in (5), usually CaCl_2 having the melting point of 780 °C is used as the molten salt. However, like binary molten salts such as $\text{CaCl}_2\text{-NaCl}$ and $\text{CaCl}_2\text{-KCl}$ and ternary molten salts such as $\text{CaCl}_2\text{-NaCl-KCl}$, at least one of other salts (for example, NaCl , KCl , LiCl , and CaF_2) can be mixed into CaCl_2 to form a multi-system molten salt.

This enables the melting point of the salt to be decreased to lower the molten salt temperature. As a result, a life of the reactor material can be lengthened, the reactor material cost can be reduced, and the Ca or salt vaporization from the liquid surface can also be suppressed.

[0041] The mixed molten salt in which NaCl is added to CaCl₂ particularly needs care among the multi-system molten salts.

Fig. 1 shows a relationship between a mixture ratio and a melting point in the binary molten salt of CaCl₂ and NaCl. The melting point of CaCl₂ is singly about 780 °C, while the melting point of NaCl is singly about 800 °C. However, when CaCl₂ and NaCl are mixed together, the melting point is decreased to about 500 °C at the minimum. The melting point of the mixed salt becomes not more than 600 °C when the mixture ratio of NaCl ranges from about 20% to about 45%.

[0042] In the multi-system mixed molten salt such as CaCl₂-NaCl and CaCl₂-NaCl-KCl containing CaCl₂ and NaCl, as shown in the following chemical formulas (d) and (e), there is a critical phenomenon in which Ca is generated at temperatures not more than 600 °C while Na is generated at temperatures more than 600 °C. That is, even if CaCl₂ is mixed in NaCl to lower the molten salt temperature to be at temperatures more than 600 °C, Ca is not generated but Na is generated in the molten salt, and the reducing reaction by Ca does not proceed.

Therefore, in the case where the molten salt temperature is decreased by mixing the NaCl with CaCl₂, NaCl is mixed such that the molten salt temperature becomes not more than 600 °C, and it is necessary to manage the molten salt at the temperatures not more than 600 °C.



[0043] As described above, it should be careful that the restriction in use exists in the multi-system molten salt containing CaCl₂ and NaCl. In the meantime, the critical phenomenon is desirable from the viewpoint of reactor material protection because the large decrease in molten salt temperature can be realized. In addition, the critical phenomenon effectively suppresses the back reaction, particularly the back reaction in which the unreacted Ca is

bonded to Cl_2 generated on the anode electrode side and Ca returns to CaCl_2 .

Specifically, in the case where the Ti particles generated on the cathode electrode side in the reactor cell is separated from the molten salt, as described above, from the view point of operation, it is rational that the Ti particles are extracted to the outside of the cell along with the molten salt after use and the Ti particles are separated from the molten salt outside the cell. In this case, usually the molten salt separated from the Ti particles is returned onto the anode electrode side in the reactor cell, the molten salt contains the unreacted Ca although the molten salt is already used, which results in the back reaction.

[0044] However, the unreacted Ca in the molten salt is replaced by Na through the reaction of the chemical formula (e), when the molten salt having the temperature not more than $600\text{ }^\circ\text{C}$ extracted from the cathode electrode side in the reactor cell is temporarily heated more than $600\text{ }^\circ\text{C}$ outside the reactor cell before the molten salt is returned to the anode electrode side in the reactor cell. Unlike Ca, Na is not dissolved in the molten salt but Na is separated from the molten salt, so that Na can be separated and removed from the molten salt.

Therefore, when the molten salt is returned to the cathode electrode side in the reactor cell after Na is separated and removed, even if the molten salt temperature is lowered to $600\text{ }^\circ\text{C}$ or less on the anode electrode side in the reactor cell, the reaction of the chemical formula (d) does not progress to block the Ca regeneration because Na is removed.

[0045] That is, in the multi-system molten salt containing CaCl_2 and NaCl , Ca is dissolved in the molten salt while Na is not dissolved in the molten salt. When the molten salt temperature exceeds $600\text{ }^\circ\text{C}$, Na is generated instead of Ca. When the two phenomena are combined, the unreacted Ca contained in the molten salt after use can be decreased to effectively suppress the back reaction caused by the unreacted Ca and the decrease in current efficiency.

[0046] As stipulated by the production method described in (7), desirably the average size of the generated Ti particles of Ti alloy particles ranges from 0.5 to 50 μm . After the Ti or Ti alloy particles are generated in the molten salt, the Ti or Ti alloy particles are extracted from the reactor cell along with the molten salt, and the Ti or Ti alloy particles are separated from the molten salt. The Ti or Ti alloy particles having the sizes not more than 50 μm can be fluidized along with the molten salt. When the particle size is more than 50 μm , it is difficult that the Ti or Ti alloy particles are extracted from the reactor cell along with the molten salt. Unless the Ti or Ti alloy particles are not less than 0.5 μm , it is difficult that the Ti or Ti alloy particles are separated from the molten salt after the extraction.

[0047] 2. Embodiment modes of Method according to the Invention

Embodiment modes of the present invention will be described below with reference to the drawing.

Fig. 2 is a block diagram showing a Ti metal production apparatus to which a first embodiment mode of the present invention can be applied.

A reactor cell 1 in which the reducing reaction and the electrolytic reaction concurrently occur is used in the first embodiment mode. The reactor cell 1 holds the Ca-rich molten CaCl_2 in which the relatively large amount of Ca is dissolved as the molten salt. CaCl_2 has the melting point of about 780 $^{\circ}\text{C}$, and the molten salt of CaCl_2 is heated to at least the melting point thereof.

[0048] In the reactor cell 1, the molten CaCl_2 which is of the molten salt is electrolyzed by passing the current between an anode electrode 2 and a cathode electrode 3, the Cl_2 gas is generated on the side of anode electrode 2, and Ca is generated on the side of cathode electrode 3. The inside of the reactor cell 1 is divided into the anode electrode side and the cathode electrode side by a membrane 4. The membrane 4 is formed by a porous ceramic thin plate, and the membrane 4 blocks the movement of Ca generated on the side of the

cathode electrode 3 toward the side of the anode electrode 2 while permitting the molten salt to be moved.

In the reactor cell 1, the gaseous TiCl_4 is injected in the dispersive manner into the molten salt on the cathode electrode side in the cell in parallel with the electrolysis of the molten salt. Therefore, the injected TiCl_4 is reduced to generate the particulate metallic Ti by the Ca dissolved in the molten salt. The generated Ti particles move downward by the specific gravity difference and accumulate at the bottom on the cathode electrode side in the reactor cell 1.

[0049] The Ti particles accumulating at the bottom on the cathode electrode side of the reactor cell 1 are extracted from the reactor cell 1 along with the molten salt existing at the bottom of the reactor cell 1, and the Ti particles and the molten salt are sent to a Ti separation step. In the Ti separation step, the Ti particles and molten salt discharged from the reactor cell 1 are separated from the molten salt. Specifically the Ti particles are compressed to squeeze the molten salt. The Ti particles obtained in the Ti separation step is melted and formed in a Ti ingot.

On the other hand, the molten salt separated from the Ti particles in the Ti separation step is designated as the molten salt after use in which Ca is consumed to decrease the Ca concentration. The molten salt separated in the Ti separation step, along with other molten salt after use separately extracted from the reactor cell 1, is introduced to the anode electrode side in the reactor cell 1.

[0050] Ca in the molten salt is consumed on the cathode electrode side in the reactor cell 1 as the Ti particles are generated by the reducing reaction. However, Ca is generated near the surface of the cathode electrode 3 in the cell by the electrolysis which proceeds concurrently in the cell, and the consumed amount of Ca is replenished by Ca generated through the electrolysis. That is, TiCl_4 supplied into the molten salt is sequentially reduced in a direct manner

by Ca generated near the surface of the cathode electrode 3.

On the other hand, the molten salt after use is sequentially introduced from the Ti separation step on the anode electrode side in the reactor cell 1. Therefore, a unidirectional flow of the molten salt is formed
5 from the anode electrode side toward the cathode electrode side in the reactor cell 1 to avoid the flow of Ca generated on the cathode electrode side into the anode electrode side. In the first embodiment mode shown in Fig. 2, the membrane 4 is provided to divide the inside of the reactor cell 1 into the anode electrode side and the cathode electrode side. The combination of the
10 provision of the membrane and the operation creating the unidirectional flow further effectively suppresses the back reaction and the decrease in the current efficiency caused thereby.

[0051] The Cl_2 gas generated on the side of the anode electrode 2 in the reactor cell 1 is sent to a chlorination step. In the chlorination step, the Cl_2
15 gas is caused to react with TiO_2 and carbon (C) (chlorination) to generate TiCl_4 which is of the Ti raw material. The generated TiCl_4 is introduced to the reactor cell 1, and TiCl_4 is used in a circulating manner to generate the Ti particles by the Ca reduction.

Thus, in the first embodiment mode, the Ti particle generation by the
20 Ca reduction, i.e., the Ca consumption and the Ca replenishment by the electrolysis are concurrently performed in the reactor cell 1. Therefore, it is not necessary to perform the Ca replenishment and Ca retrieval in the solid state, and the high-quality Ti particles can be produced continuously and economically through the Ca reduction. The reactor cell 1 is used as both the
25 reducing cell and the electrolytic cell, so that there is an economical advantage in the facilities. The flow of Ca generated on the cathode electrode side into the anode electrode side is avoided in the reactor cell 1, so that the back reaction in which Ca reacts with the Cl_2 gas generated on the anode electrode side can be prevented.

The molten salt temperature is managed to be more than the melting point (about 780 °C) of CaCl_2 in each step.

[0052] Fig. 3 is a block diagram showing a Ti metal production apparatus to which a second embodiment mode of the present invention can be applied.

5 The second embodiment mode differs from the first embodiment mode in the following points. That is, a mixture of CaCl_2 and NaCl is used as the molten salt. In the mixture, CaCl_2 and NaCl are mixed together at a mixture ratio in which the melting point of the mixture becomes not more than 600 °C. The mixed molten salt is held at temperatures of not more than 600 °C in the
10 reactor cell 1, and the mixed molten salt is held at temperatures of more than 600 °C in a separation cell 5 used in the Ti separation step.

[0053] Because the molten salt is held at temperatures of not more than 600 °C the reactor cell 1 in which the reducing reaction and the electrolytic reaction concurrently occur (namely, low-temperature reduction and
15 low-temperature electrolysis are performed), Ca which is of the reducing agent exists in the molten salt (see chemical formula (d)), even if the molten salt is the mixed molten salt of CaCl_2 and NaCl . Therefore, the reducing reaction by Ca and the Ca generation and replenishment by the electrolysis are concurrently performed. The low-temperature reduction and the
20 low-temperature electrolysis are performed in the reactor cell 1, so that the reactor material life can be lengthened to decrease the reactor material cost.

Because Ca has the higher reactivity than that of Mg, the development of the reactor material which can withstand Ca for a long period is the important technological problem in the mass production of Ti or Ti alloys.
25 The molten salt temperature is decreased to reduce the impact on the reactor material during the operation by the low-temperature reduction and the low-temperature electrolysis, so that the present invention largely contributes to solve the problem of the reactor material life.

[0054] On the other hand, in the Ti separation step, the molten salt and the

Ti particles are extracted from the reactor cell 1 into the separation cell 5, or the molten salt is independently extracted from the reactor cell 1 into the separation cell 5. The molten salt extracted from the reactor cell 1 is already used, and the molten salt contains the slight amount of unreacted Ca although
5 Ca is consumed. When the molten salt containing the unreacted Ca is returned to the side of the anode electrode 2 in the reactor cell 1, the unreacted Ca reacts with the Cl_2 gas generated on the side of the anode electrode 2 to generate the back reaction.

However, in the second embodiment mode, unlike the reactor cell 1,
10 the molten salt is held at temperatures of more than 600 °C in the separation cell 5, so that the unreacted Ca slightly contained in the molten salt is replaced by Na (see chemical formula (e)). Unlike Na, Ca is not dissolved in the molten salt, Ca is separated to float on the molten salt, and Ca is removed from the molten salt. The molten salt in which the unreacted Ca (namely, reducing
15 agent metal) is removed is sent to the side of the anode electrode 2 in the reactor cell 1, and the molten salt temperature is managed to be not more than 600 °C. Because Na is removed as described above, the reaction of the chemical formula (d) does not occur, and Ca is not regenerated. Therefore, the back reaction caused by the mixture of the unreacted Ca and the decrease
20 in current efficiency caused by the back reaction are blocked.

[0055] That is, the Ti separation step in the second embodiment mode also functions as the Na separation step (reducing agent separation step), and the unreacted Ca in the molten salt returned to the reactor cell 1 is removed by previously replacing the unreacted Ca with Na, which enables the rational and
25 economical operation to be realized. Na separated from the molten salt in the separation cell 5 is sent back to the side of the cathode electrode 3 in the reactor cell 1, Na returns to Ca (see chemical formula (d)) by managing the melt at temperatures of not more than 600 °C, and Na is reused for the reducing reaction.

The molten salt temperature in the separation cell 5 can obviously be set at the same temperature as the reactor cell 1 whose temperature is not more than 600 °C. In this case, there is an advantage from the viewpoint of reactor material durability while the unreacted Ca cannot be removed.

5 [0056] Fig. 4 is a block diagram showing a Ti metal production apparatus to which a third embodiment mode of the present invention can be applied.

The third embodiment mode differs from the first embodiment mode in a structure of the cathode electrode 3. That is, the third embodiment mode is a configuration example of the Ti metal production apparatus in which the
10 production method described in (2) can be performed. The cathode electrode 3 is made of an electroconductive porous material in the third embodiment mode while the cathode electrode 3 is made of the solid metals such as Fe and Ti in the first embodiment mode. Specifically, the cathode electrode 3 is made of the electroconductive porous material such as a Ti sintered porous material and a
15 Fe sintered porous material. In the third embodiment mode, the TiCl_4 gas which is of the Ti raw material is supplied into the molten salt on the side of the cathode electrode 3 in the reactor cell 1 through the porous cathode electrode 3 (namely, flows through the inside of the porous material).

[0057] In the case where TiCl_4 is supplied into the molten salt on the cathode
20 electrode side in the reactor cell 1, it is necessary that TiCl_4 is supplied to a portion near the surface of the cathode electrode 3 as much as possible. Because the Ca generation by the electrolysis is performed near the surface of the cathode electrode 3, the reaction efficiency is increased when TiCl_4 is supplied to the portion near the surface of the cathode electrode 3. The
25 productivity of the Ti particles is further improved by adopting the third embodiment mode.

In the third embodiment mode, similarly to the second embodiment mode, the mixed molten salt of CaCl_2 and NaCl can be used, the low-temperature reduction and low-temperature electrolysis can be performed

with the mixed molten salt of CaCl_2 and NaCl , and the unreacted Ca (reducing agent) can be separated at high temperatures.

[0058] In the first to third embodiment modes, carbon or graphite is used as the anode electrode 2 to generate the Cl_2 gas.

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INDUSTRIAL APPLICABILITY

[0059] According to the method for producing Ti or Ti alloys through the reduction by Ca according to the present invention, the feed rate of TiCl_4 which is of the raw material can be enhanced, and the high-purity Ti or Ti alloys can
10 continuously be produced. In the reactor cell, the reducing reaction and the electrolytic reaction can concurrently be caused to proceed, and Ca consumed in the reducing reaction can be replenished by the electrolytic reaction, so that it is not necessary to singly handle Ca . The back reaction caused by Ca can also effectively be suppressed.

15 Accordingly, the method according to the present invention can effectively be utilized as means for efficiently and economically producing the high-purity Ti metals or Ti alloys, and the method according to the present invention can widely applied to the industrial Ti or Ti alloy production method.